

CHAPTER 6

CONCLUSIONS

Batch Equilibrium Studies

This research was primarily motivated by the need to provide finer resolution of the spatial variability of distribution coefficients in sedimentary interbed below the RWMC than has been previously determined from homogenized composite samples for transport modeling. The primary objective of the research was to characterize sorption for chromium-51, uranium-233, neptunium-237, and americium-241 in depth discrete sedimentary interbed grab samples from beneath the RWMC and to examine its variability among the soil samples. A secondary objective was to examine the effect of bicarbonate, sulfate, and fluoride on sorption behavior.

The major conclusion that can be drawn from this research is that sorption behavior for uranium and neptunium was nonlinear at the aqueous phase concentrations examined in these studies. Consequently, a linear distribution coefficient sorption model may be inappropriate to characterize sorption behavior in the traditional transport modeling approach. The Freundlich sorption model was shown to characterize the contaminants' sorption behavior well over the aqueous phase concentration range examined here. Therefore, the Freundlich model may be a more suitable approach to characterize sorption behavior than the linear model over aqueous concentrations similar to those examined here.

Secondly, the sorption affinity for uranium and neptunium was observed to vary by less than an order of magnitude among the soils. The variations observed in this research were small given that in highly heterogeneous subsurface environments soil properties may vary by several orders of magnitude. Consequently, the observed uniformity in sorption affinity among the soils suggests that the use of a finer spatial scale in transport modeling may not be necessary.

Statistical analyses were performed to determine if sorption behavior was correlated with common gross soil properties. Specific correlations with surface area, cation exchange capacity, clay content, and extractable metals content were strong for some of the soil properties. However, the strong correlations were likely a result of the small ranges of soil properties, and probably represent scatter about a small range of a possible relation.

Ligand studies were performed to examine the effect of bicarbonate, sulfate, and fluoride on sorption behavior for uranium and neptunium. Uranium is known to form soluble carbonate species. Consequently, the observed losses of uranium were likely the result of precipitation in the absence of sufficient carbonate. The strong influence of carbonate on uranium behavior masked the effects of sulfate and fluoride in these studies and no conclusions regarding their specific effects were drawn.

The sorption behavior of neptunium was similar among the three groundwater simulants suggesting that carbonate, sulfate, and fluoride had little effect. Additionally, geochemical speciation modeling indicated that NpO_2^+

dominated neptunium speciation. Therefore, NpO_2^+ was probably the dominant sorbing neptunium species onto the INEEL soils.

The loss of aqueous phase chromium was typically lowest for samples with the highest solids concentration. Additionally, large losses of chromium were observed in the blanks (no soil). Apparent distribution coefficients were calculated for samples with the highest solids concentration since these samples were thought to minimize the effect of precipitation because of their large number of potential sorption sites. Apparent distribution coefficients were relatively small for these samples on all soils suggesting that chromium's affinity for the soils was small.

Solubility studies indicated substantial loss of americium under the experimental conditions examined in these studies. Consequently, partitioning studies were not performed for americium because a sufficient range of aqueous phase concentrations could not be examined. The loss of americium may have resulted from the precipitation of $\text{AmOHCO}_3(\text{c})$, which is predicted to be the solubility limiting species.

Environmental Significance

The major contribution of this work to the understanding of the transport of radionuclides beneath the RWMC is that the use of a linear distribution coefficient model in traditional transport modeling may not be appropriate for uranium and neptunium at the aqueous concentration ranges examined here. A more appropriate approach may be the use of the Freundlich sorption model in place of the linear model to characterize the nonlinear contaminant retardation to

the geologic media that was observed in these studies. However, caution should be used when applying the Freundlich model since the flexibility of the model parameters may not be able to characterize contaminant sorption outside of the experimental aqueous concentration ranges examined in these studies. Additionally, nonlinear sorption indicates a decreasing rate of sorption with increasing aqueous phase concentrations. As the aqueous concentration of a contaminant increases, its mobility increases relative to its mobility at a lower aqueous concentration, allowing the contaminant to travel further than predicted with a linear sorption model.

Secondly, the variation in sorption affinity among the soil samples was relatively small suggesting that sorption behavior may be more uniform than previously suggested. This conclusion suggests that the use of a finer spatial scale for transport modeling may not be necessary.

Third, perturbations in groundwater chemistry may influence contaminant mobility in various distinct ways. For uranium, changes in carbonate concentrations should have a strong influence on mobility. Uranium should be more mobile in carbonate environments. For neptunium, carbonate, sulfate, and fluoride should exert little influence on its mobility since the results of this research suggest NpO_2^+ is likely to be the dominant sorbing neptunium species at the INEEL.

Finally, precipitation of insoluble americium carbonates is well documented in the literature and supported by this research. Therefore, precipitation will likely exert more influence on americium mobility at the INEEL

than retardation by the geologic media. Additionally, trivalent chromium sorption is expected to be small. Precipitation of chromium hydroxides is also well documented and is likely to be more influential in controlling chromium mobility than sorption.

Recommendations

With respect to future research, the following recommendations are made:

1. Experimental plans need to be developed to examine the sorption behavior of chromium and americium on INEEL soils in batch tests. These may include the quantification of material in all compartments of the experimental setup. For chromium, the use of a stable isotope may also be required given the short half-life of ^{51}Cr .
2. Continued work should elucidate the effect of groundwater ligands on contaminant sorption.
3. Sorption behavior should be modeled using a surface complexation model that is based on a more mechanistic approach than the empirical models utilized in this research.
4. Future work should involve the examination of surface sites to elucidate actual species and mechanisms of contaminant sorption to the INEEL soils in support of the surface complexation modeling.